VOLATILE ABUNDANCES OF APATITE IN CK AND R CHONDRITES: IMPLICATIONS FOR APATITE VOLATILE RECORDS IN OXIDIZED AND THERMALLY ALTERED CHONDRITE PARENT BODIES.

F. M. McCubbin^{1*}, J. A. Lewis¹, J. J. Barnes², J. W. Boyce¹, J. Gross^{1,3}, M. C. McCanta⁴, P. Srinivasan⁵, B. A. Anzures⁶, N. G. Lunning¹, S. M. Elardo⁷, L. P. Keller¹, T. C. Prissel¹, and C. B. Agee⁵; ¹NASA Johnson Space Center, Houston, TX 77058; ²Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721; ³Department of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ 08854; ⁴Department of Earth and Planetary Science, Institute of Meteoritics, University of Tennessee, Knoxville, TN 37996; ⁵Dept. of Earth and Planetary Science, Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87123; ⁶Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058; ⁷Department of Geological Sciences, University of Florida, Gainesville, FL 32611.*francis.m.mccubbin@nasa.gov

Introduction: The mineral apatite $[Ca_5(PO_4)_3(F,Cl,OH)]$ is one of the primary mineralogical reservoirs for phosphorus on Earth [1], and it is a common phosphate mineral within a broad range of extraterrestrial samples [e.g., 2]. Naturally occurring apatite hosts F, Cl, and OH as essential structural constituents, and all three make up the apatite fluorapatite, endmembers chlorapatite, hydroxylapatite, respectively. The presence of apatite in chondrite parent bodies indicates that apatite may hold a record of volatiles and their associated processes during the nascent stages of planetesimal formation and evolution [3].

Apatite is commonly cited as a primary condensate from the nebula at 710-734 K (fluorapatite), which defines the 50% condensation temperature of fluorine [4-5]. The 38–50% condensation temperature for Cl is defined at 470–472 K (chlorapatite) [5-6]. At 850–1285 K, the physicochemical conditions within the nebula favor the formation of phosphides and phosphorus components in Fe-rich metal on the basis of fO2 [e.g., 7]. Phosphides begin to oxidize to phosphates at about 850 K [7]. However, apatite within chondrites may not be condensates from the nebula. In fact, apatite in ordinary chondrites form through metasomatic processes involving the oxidation of P in metal to form merrillite, followed by metasomatism of merrillite by Cl-rich, H₂O-poor fluids to form apatite [8-10]. Ordinary chondrites are formed from reduced precursor materials that preclude a nebular origin of apatite, however some apatite-bearing chondrite parent bodies are more oxidized, and the origin of apatite in those materials is less clear.

Previous work on apatite in chondrites have focused on the reduced and thermally altered ordinary chondrites. In the present study, we characterize apatite from the oxidized thermally altered Rumuruti-type (R) chondrites and carbonaceous Karoonda-type (CK) chondrites. We recently used these data to form a more complete survey of apatite compositions from thermally metamorphosed chondrite parent bodies [3]. Here, we highlight a portion of that study to discuss what volatile

records may be captured by apatite in chondrite parent bodies broadly.

Methods: Major and minor element compositions of apatite were acquired by electron probe microanalysis using a JEOL 8530 field emission electron microprobe from NASA Johnson Space Center using methods similar to those described in [3, 11].

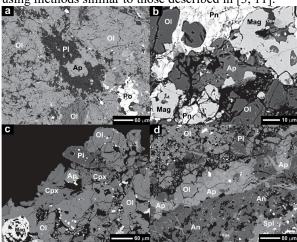


Figure 1. High-resolution back-scattered electron images of apatite from chondrites a) PCA 91002 (R3.8-6) b) Karoonda (CK4) c) DAV 92300 (CK4) d) Maralinga (CK4). All phases present are identified, and the phase abbreviations are indicated as follows: An = anorthite, Ap = apatite, Chr = chromite, Cpx = clinopyroxene, Fas = fassaite, Mag = magnetite, Opx = orthopyroxene, Ol = olivine, Pl = plagioclase, Pn = pentlandite, Po = pyrrhotite, Spl = spinel.

Results: Apatite in CK chondrites exhibit four textural occurrences, including (1) within magnetite-sulfide chondrules, (2) as discrete grains within CK matrix, (3) anhedral-subhedral oikocrysts that fill the interstitial space between olivine grains, and (4) within anorthite-olivine-spinel-magnetite CAIs in the anomalous CK4 Maralinga (Figure 1). The apatite in CK meteorites is predominantly Cl-rich and F-poor but exhibit a large halogen deficiency that implies a large range in Cl/OH ratios (Figure 2).

Apatite exhibits a variety of textures in R chondrites, including as (1) discrete grains with subhedral-anhedral habit, (2) anhedral-subhedral intergrowths with silicate

phases like olivine, and (3) as anhedral-subhedral grains in close association with Fe-Ni sulfides (Figure 1). Many of the apatite in R chondrites host smaller oxide and/or sulfide phases. The apatite in R chondrite meteorites are predominantly F-poor with variable amounts of Cl ranging from chlorapatite to non-halogen dominant apatite. The large halogen deficiency in many R chondrite apatite implies a large range in Cl/OH ratios (Figure 2).

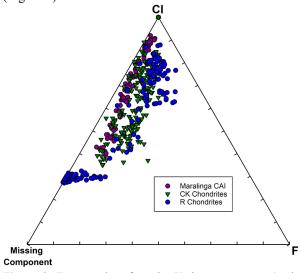


Figure 2. Ternary plot of apatite X-site components (mole fraction) from all chondrites analyzed in the present study. The missing component was calculated based on 1-F-Cl= missing component.

Discussion: Both fluorapatite and chlorapatite are reported to form during nebular condensation [4-5, 7]. Fluorapatite is thought to have condensed out of the nebula at 710-734 K, prior to the formation of chlorapatite at about 470 K. However, the results of this study show that apatite from CK and R chondrite predominantly chlorapatite meteorites are hydroxylapatite (Figure 2, [3]), in contrast to the Clrich, F- and OH-poor apatite in ordinary chondrites [8-10]. Consequently, if fluorapatite condensed from the nebula, it did not survive subsequent nebular and/or parent body processing. It is unclear whether (1) apatite compositions from R and CK chondrites evolved towards Cl- and/or OH-rich compositions with decreasing temperature through reactions with nebular gas prior to incorporation into their respective parent bodies and/or (2) the X-site compositions of apatite observed in CK and R chondrites are the result of parent body processes alone.

This study represents the first comprehensive dataset on the halogen abundances of apatite from R and CK chondrites [3]. In contrast to apatite in ordinary chondrites, our data indicate a substantial missing component in the X-site of CK and R chondrite apatite

that could be attributed to OH. One of the fundamental questions in planetary science is the origin of H₂O and how it was distributed within the circumstellar disk within the first 4 Ma of the birth of our solar system. To answer this question, we need to investigate the earliest-formed samples of our solar system, which includes a variety of chondrites and achondrites. Given the likely record of H₂O in apatite from R and CK chondrites, these samples have untapped potential to provide important constraints on the origin of H₂O within the inner (R chondrite) and outer (CK chondrite) solar system reservoirs through H-isotopic analyses.

Although encouraging, the missing components in CK and R chondrite apatite have not been measured and are only presumed to be OH. Such caution is particularly warranted because the missing component detected in the X-site of apatite from ordinary chondrites was much larger than the measured abundances of OH [8-9]. Nonetheless, there is reason to be cautiously optimistic about the attribution of the missing X-site components of CK and R chondrite apatite to OH. In particular, the H₂O-rich nature of fluids on the R chondrite parent body is supported by the presence of H₂O-rich amphibole and biotite within a subgroup of R chondrites [12-13]. Moreover, both CK and R chondrites are more oxidized than ordinary chondrites. The R chondrites exhibit fO2 values as high as the favalite-magnetite-quartz (FMQ) buffer, and the CK chondrites exhibit fO2 values up to FMQ +4.5 [14]. These fO_2 values would correspond to high fH₂O/fH₂ ratios of any parent body fluids [e.g., 14], making oxidized hydrogen available for incorporation into minerals during thermal metamorphism. In contrast, the metal-rich ordinary chondrites likely had parent body fluids with low fH₂O/fH₂ ratios [15-18], which would limit OH incorporation into minerals during thermal metamorphism. In summary, the apatite in CK and R chondrites are prime targets for gaining additional information about the origin of H₂O in our solar system.

References: [1] Piccoli and Candela (2002) *RiMG* 48, 255-292 [2] McCubbin and Jones (2015) *Elements* 11, 183-188. [3] McCubbin et al. (2023) *Am Min* In press [4] Fegley and Schafer (2010) <u>Cosmochemistry</u> 347-377 [5] Lodders (2003) *Ap J* 591, 1220-1247. [6] Wood et al. (2019) *Am Min*104, 844-856 [7] Pasek (2019) *Icarus* 317, 59-65. [8] Jones et al. (2014) *GCA* 132, 120-140. [9] Jones et al (2016) *Am Min* 101, 2452-2467 [10] Lewis and Jones (2016) *MAPS* 51, 1886-1913. [11] McCubbin et al (2021) *GCA* 314, 270-293 [12] McCanta et al (2008) *GCA* 72, 5757-5780. [13] Gross et al (2013) *LPSC* 44 #2212 [14] Righter and Neff (2007) *Polar Science* 1, 25-44 [15] Sharp et al (2013) *EPSL* 380, 88-97 [16] Sutton et al (2017) *GCA* 211, 115-132 [17] McCubbin and Barnes (2019) *EPSL* 526, 115771 [18] Alexander (2017) *PTRS-A* 375